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PROBLEMS OF APPLICATION OF UNMOLDED REFRACTORIES

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Problems that restrain wide application of unmolded refractories are considered: a need for close cooperation between experts in binding materials and experts in ceramics and refractories; logistic problems, especially implementation of engineering support of the product. A need is noted for organizing the testing of deformation properties of refractory materials under conditions equivalent to their service conditions. Taking into account single or short-series production of such articles, it is most convenient to produce them at small or medium-sized companies oriented to regional markets.

Refractory concrete (concrete with a refractory ceramic filler and a binder passing in heating into a refractory compound) that belongs to the category of unmolded refractories is finding increasingly wide application in industry [1 – 6]. This material offers a number of advantages to manufacturers and consumers. Consumers of such concrete have 1.5 – 4 times savings in labor needed to construct or repair thermal plant lining, mechanization of construction and destruction of lining is facilitated, service characteristics of thermal plants are improved, and it becomes possible to create continuous, seamless, large-brick lining, which makes it possible to decrease by 50% the consumption of refractories per ton of product produced in the plant lined with this material. Unmolded refractories are successfully used in hot repair of furnaces. Such materials open up vast possibilities for adapting their composition, structure, and properties to service conditions. They can be used to make products of a complex configuration instead of profiled refractories produced by the firing technology. They give much more freedom to designers of thermal plants.

Manufacturers also receive substantial advantages in producing refractory concrete. This process is simpler than production of traditional refractories, whereas capital investments are 40 – 50% lower. Labor consumption per ton of refractory product decreases, since such operations as compression of intermediate products and their drying and firing can be eliminated. The latter leads to 5 – 6-fold savings in power consumed. The properties of unmolded refractories contribute to decreasing storage space, inventory, and storage period.

Despite the obvious advantages, unmolded refractories are insufficiently extensively used instead of traditional refractories. This is due to a number of objective and subjective factors.

The purpose of this article is to analyze reasons impeding expansion in production and use of unmolded refractories.

A specific feature of production and use of refractory concrete is that it involves both the technology of binding materials (mixing of components, molding, and curing at room temperature or low-temperature treatment) and the technology of ceramics (processes of high-temperature firing of refractory material may take place directly inside a furnace). All this calls for close coordination of engineers who have different, although close, specializations, and such situations always create additional problems. As a consequence, research and development of unmolded refractories was usually in the background for research centers engaged in developing binding materials or ceramics.

Experts in binding materials are well aware of continuous changes in the properties of binding materials and concretes, whereas such processes in ceramics are not as perceptible. This creates difficulties for consumers who are used to traditional refractories. Despite the simplicity of application, one should deeply understand the processes occurring in unmolded refractoriness. For instance, the ambient medium (temperature, moisture, composition of the gas medium) influences the curing processes. Properties of liquids used for mixing (water, chemical and other binders) may be significant as well. Ignorance of these factors may result in destruction of such materials at the consumer's place and may ruin one's despite to use unmolded refractories, despite their advantages.

No less important is the behavior of unmolded refractories under high-temperature treatment. After the first treatment inside a furnace, the material is transformed into a ceramic and its subsequent heating produces less significant

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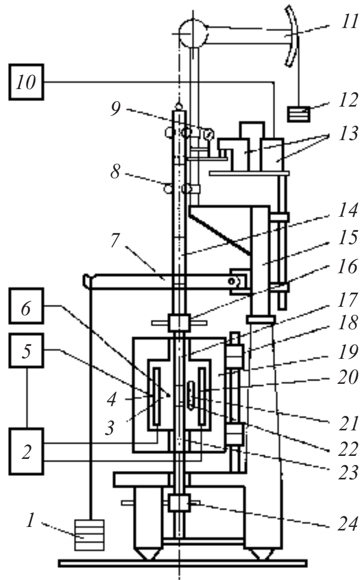

Fig. 1. Fundamental scheme of a single-position set: *1*) loads; *2*) control system; *3*, *4*) thermocouples; *5*, *6*) temperature control and regulation devices; *7*) lever; *8*) guiding rolls; *9*) indicator; *10*) inductive sensor; *11*) cable; *12*) counterbalance load; *13*) recorder; *14*) rod; *15*) post; *16*, *24*) cooling jackets; *17*, *23*) loading rods, *18*) hinge, *19*) furnace; *20*) heaters; *21*) peephole; *22*) sample.

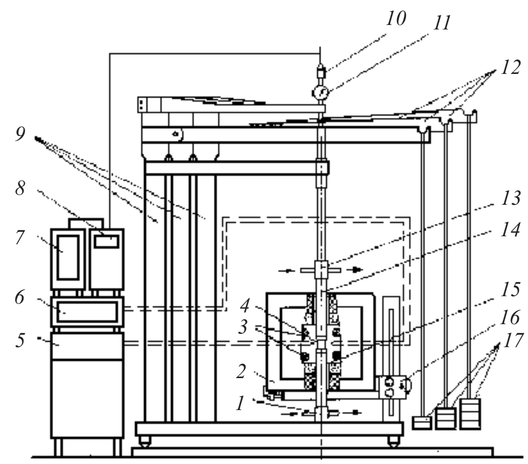

Fig. 2. Fundamental scheme of a three-position set: *1*, *13*) cooling systems; *2*) furnace; *3*) heaters; *4*) sample; *5*, *16*) temperature control and regulation devices; *6*, *7*) deformation monitoring and recording devices; *8*) posts; *9*) rod; *10*) inductive sensor; *11*) indicator; *12*) lever system; *14*, *15*) loading rods; *17*) loads.

changes in its composition, structure, and properties. Volume changes (primarily, shrinkage) occurring in this case are capable of provoking cracks and even destruction of the articles. This is especially significant in making large-size products, for instance, continuous furnace lining, which is very promising.

It is very important to know variations in the strength and deformation properties of materials undergoing a first heat treatment. At a temperature at which the binder has not yet transformed into ceramics, the strength of material depends on compounds formed in curing of the binder. A temperature rise usually facilitates decomposition of these compounds and the strength drops. The decrease in strength may be so significant that the lining structure may be destroyed. With a further temperature rise, strength also starts growing due to sintering processes. Hydraulically cured binders are especially dangerous with respect to a strength decrease. Consequently, producers tend to decrease their content and to use low- and ultralow-cement refractory concretes [5].

There are binders whose strength decreases but little under heating. These are binders based on sodium silicate glass, organosilicon polymers, silica sol, highly concentrated binding suspensions [6], and phosphate compounds (orthophosphoric acid, aluminophosphates, aluminochromium-phosphates, and other binders). Phosphate binders [3, 4, 7 – 9] have a number of advantages over hydraulic ones. They ensure high strength of intermediate pieces at room temperature. The strength of articles varies little with rising temperature. With a correctly chosen granular composition and in thermal treatment up to 600°C they ensure water resistance and a virtually constant volume in products subsequently heated to 1000 – 1200°C, which is sufficient for many application areas. At the same time, use of orthophosphoric acid requires compliance with certain safety rules.

The problems of unmolded refractories in the present paper are mainly considered for production and use of concrete based on phosphate binders, taking into account research carried out at the Bashkirian Research and Design Institute for Building Materials Industry (BashNIPIstrom).

To identify the deformation behavior of unmolded refractories in heating, researchers at the BahNIPIIstrom have developed plants that are schematically represented in Figs. 1 and 2. These sets make it possible to register size variations in refractory samples up to a temperature of 1550°C under loading from 0.04 to 5.0 MPa using the uniaxial compression method [10, 11]. Size variations were determined using a clockwise mechanical indicator, an inductive sensor, or a V-630 cathetometer.

The single-position plant (Fig. 1) was used to test cylindrical samples of diameter 36 mm and 50 mm high. To eliminate the nonuniform deformation zone formed due to the effect of loading rods, samples 76 mm high were tested as well (Fig. 3). Radial holes were made at the side of a cylindrical sample at a distance of 18 mm from the end faces of the sample, in which corundum rods 1.0 – 1.5 mm in diameter were inserted, the rods protruding beyond the lateral surface of the cylinder. These rods were used to measure deformation employing a cathetometer. The measurement error did not exceed 10%.

The three-position plant (Fig. 2) can be used for simultaneous measurement of three cylindrical samples 20 mm in diameter and 30 mm high made of various materials. Testing can be implemented under constant or variable loads and

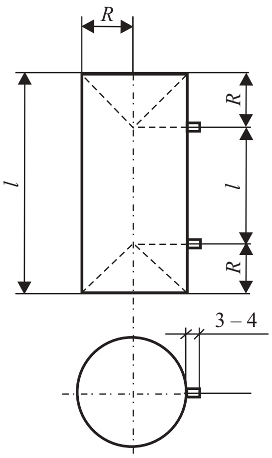

Fig. 3. A sample with corundum rods to measure deformation with a cathetometer.

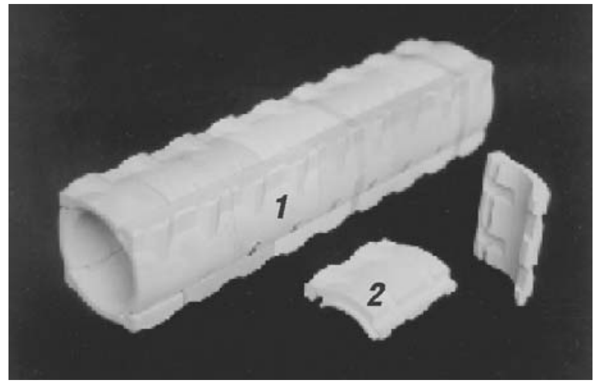

Fig. 4. Ceramic pipe of AICELIN furnace assembled (*1*) and its elements (*2*).

temperatures. The estimated error does not exceed 2.5% for a deformation interval of 0.2 – 10.0% and 25% for 0.006 – 0.200%.

Studies of the deformation behavior of unmolded refractories are needed to select optimum heat-treatment conditions, which ensure the required resistance of the material to high-temperature creep [9].

Testing carried out on these plants not only makes it possible to develop new refractory composites, but also to control the deformation properties of the product. These devices have been successfully used to fill the orders of customers. Knowing the service conditions of a particular refractory product, technologists make a decision on its production method. Sometimes, for instance, in repairing furnace lining, it is advisable to manufacture the product at the customer's facility and to implement high-temperature treatment of the product directly during a first heating of the furnace. Analysis of materials performed on this set makes it possible to select optimum conditions for such heat treatment, to coordinate it with possibilities of the thermal plant in repair, and to verify the behavior of the material under loads expected in service.

In other cases it is more convenient to heat-treat products at the manufacturer's. In this case, testing on the set makes it possible to select a minimum heat-treatment temperature sufficient to prevent undesirable changes in the properties of the refractory product during the first heating at the customer's. This is more convenient for the manufacturer as well as for the customer in cases of small-sized articles.

The availability of the measuring sets and research on the behavior of unmolded refractories in heating made it possible to develop an efficient plastic molding method based on phosphate binders. It is known [12] that a mixture heated up to 140°C acquires high plasticity, which enables one to mold articles by drawing or additional compression. Figures 4 – 6 show articles produced with this technology.

In making single or short-run ceramic articles, the most substantial problem is making molds for articles of complex configurations. The cost of such molds usually exceeds the cost of the ceramic articles. A customer is not always able to supply or produce such a mold. Using unmolded refractories considerably simplifies this problem. A mold can be made not only of metal, but also of polymer, wood, gypsum, or cement. Such molds are significantly cheaper, but they only allow for producing one or a few articles. This has been corroborated by the practical experience of making articles based on phosphate binders.

An advantage of unmolded refractories is the possibility of making large-sized lining elements, for instance, continuous furnace lining. Strength and preservation of size under heat treatment are ensured by the granular composition of the filler and the composition of new formations synthesized in chemical binding of particles in the intermediate product. Phosphate binders are especially convenient, since the strength of articles varies little in heating. Unilateral heating of furnace lining results in the fact that the structure of the material adapts to the heating conditions. Accordingly, such linings have a longer service life. At the same time, the strength of the material at a distance from the hot side of the lining decreases not so significantly, as in hydraulically cured cements.

Usually it is not economically efficient for large producers to fill single-item or short-run orders, which are better implemented by small or medium-sized companies, one of which is BashNIPIstrom. Companies in the oil, chemical, and machine-building sectors often experience big problems in repairing furnaces and replacing worn refractory parts. Although the cost of refractories is relatively low compared to the cost of the whole furnace, these elements frequently determine the furnace parameters. The possibility of making complex-shaped articles from refractory concrete based on phosphate binders makes it possible to satisfy most customer requirements.

The BashNIPIstrom has experience in producing special concrete articles based on silicon nitride and phosphate binders: crucibles resistant to various aluminum melts; metal pipelines for transportation of aluminum melts in foundry machines and plants; radiation ceramic pipes in cementing and nitrocementing plants (Figs. 4 – 6), insulating nozzles of

Fig. 5. Burner stone element for burners GDU-50 obtained by ramming.

Fig. 6. High-temperature paste for lining and repair of steam boilers of sea vessels.

copper holders in equipment for subsurface metal cutting. Several industrial sectors in the Republic of Bashkortostan efficiently use aluminosilicate and alumina products based on phosphate binders to construct and repair refractory lining of thermal plants, such as firing cars for tunnel furnaces and furnaces for ceramic production.

Main physicotechnical properties of refractory concrete based on phosphate binder

Strength MPa:	
compressive	170 – 200
bending	15 – 20
Open porosity, %.	15 – 47
TCLE, 10^{-6} °C^{-1}	3 – 8
Thermal resistance, number of thermal cycles (1000°C – water)	Over 30
Deformation starting temperature, °C	Up to 1750
Refractoriness, °C	Up to 1800
Volume resistivity, $\Omega \cdot$ m, at temperature:	
20°C	3.7×10^{12}
500°C	3.3×10^{9}
Breakdown voltage, kV/mm	2.5 – 6.5
Dielectric loss tangent at a frequency of 10^{10} Hz	$(3...8) \times 10^{-4}$
Dielectric permeability at a frequency of 10^{10} Hz.	3.0
Apparent density, g/cm^3	1.8 – 3.2

One of the obstacles to a wider application of unmolded refractories is the fact that potential consumers, as a rule, are not familiar with the specific behavior of these refractories in molding, hardening, drying, and under high-temperature treatment. This is explainable, since refractories play an important but auxiliary role in their technologies. Furnace lining and other refractory products are often needed as single or short-run items. Taking into account the insufficient experience of potential users in working with unmolded refractories, it is necessary to provide engineering support for the refractories produced. Otherwise it is very difficult to avoid frustrating mistakes in the application of such materials, which discredits the manufacturer.

The experience of BashNIPIstrom has demonstrated that it is advisable to preheat single products made of unmolded refractories on phosphate binder at temperatures around 600°C, at which the main processes in the binder end. Such articles can be transported to a user without the risk of destruction due to a reaction with the ambient medium and/or problems related to the first heating of a thermal plant. Obviously, the manufacturer should know as precisely as possible the service conditions of the refractory product in order to give expert advice to the user. It is best when a representative of the manufacturer is present during the installation of the furnace lining. This is especially essential for the first heating of the furnace, in order to prevent destruction of articles occasioned by an excessively abrupt schedule of the first heating.

Thus, the development and use of unmolded refractories calls for closer cooperation between experts in binding materials and experts in ceramics and refractories. Taking into account that the articles considered are produced individually or in small series, it is convenient to produce them at small or medium companies. Such companies should possess plants for testing deformation properties of refractory materials in heating. The most important problem is organization of engineering support for products. One should strive to have a manufacturer's specialist present at the installation of refractory concrete lining or nonfired ceramics during their first thermal treatment in a repaired furnace. Furthermore, to reduce cost, it is advisable to target regional markets.

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